

Microscopic Theory of Cation Exchange in CdSe Nanocrystals

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Abstract

Although poorly understood, cation-exchange reactions are increasingly used to dope or transform colloidal semiconductor nanocrystals (quantum dots). We use density-functional theory and kinetic Monte Carlo simulations to develop a microscopic theory that explains structural, optical, and electronic changes observed experimentally in Ag-cation-exchanged CdSe nanocrystals. We find that Coulomb interactions, both between ionized impurities and with the polarized nanocrystal surface, play a key role in cation exchange. Our theory also resolves several experimental puzzles related to photoluminescence and electrical behavior in CdSe nanocrystals doped with Ag.

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Colloidal nanocrystals [1] with well-defined size and shape can be synthesized directly only for a few semiconductors. Each new material requires considerable effort to optimize the growth [2]. To avoid this, researchers have exploited a simple process known as “cation exchange” [3–8]. Nanocrystals (NCs) that can already be directly synthesized (e.g. CdSe) are exposed in solution to cations (e.g. Ag^+) that quickly diffuse into the lattice and replace the original cations. If this reaction goes to completion, a new crystalline material is created (e.g. Ag_2Se) with the size and shape of the initial NCs. Recently, cation exchange has also been used for another purpose: to incorporate impurities as dopants into NCs [9, 10]. Dopants can create mobile electrons and holes but their incorporation during the conventional growth of NCs has been challenging [11]. By arresting cation exchange at an early stage, a controllable number of impurities can be introduced by diffusion into premade NCs. Cation exchange is thus becoming an important route to both new and doped NCs. However, the mechanisms underlying cation exchange remain unclear. A microscopic theory could greatly extend the use of cation-exchange reactions for creating new NC materials.

The theory must explain several experimental observations for the well-studied cation exchange of Ag in $\text{Cd}E$ NCs ($E = \text{S or Se}$). (1) When sufficient Ag is added to solution, Ag_2E NCs are obtained very rapidly [3]. (2) Early attempts to halt the process and incorporate less Ag led to phase segregation, with Ag_2E nucleated at the NC surfaces [12]. (3) When individual Ag impurities were eventually incorporated [10], the NCs exhibited optical and electronic properties suggesting a transformation from a donor to an acceptor with increasing Ag concentration.

In this Letter we propose an atomistic model that explains these observations. We used density-functional theory (DFT) to calculate impurity formation energies and reaction barriers for Ag in bulk CdSe. These were then used in dynamical simulations of cation exchange in NCs at finite temperature over long times. Our simulations spanned a wide range of Ag concentrations, from light doping to complete cation exchange, and provide a single conceptual framework in which to understand the process. Our simulations show that Coulomb interactions between ions play a central role in cation exchange. Indeed, if we suppress Coulomb interactions then cation exchange does not occur. Our simulations also show that Coulomb effects underlie the unusual optical and electronic behavior of Ag-doped CdSe NCs.

We begin by considering two types of Ag impurities in bulk CdSe: interstitial Ag (Ag_{int}) and Ag substitutional on a Cd site (Ag_{Cd}) [13]. We used DFT total-energy calculations to

determine the equilibrium geometries and stable charge states of each. Total energies and forces were calculated within the generalized-gradient approximation of Perdew, Burke, and Ernzerhof (PBE) [23] using projector-augmented-wave potentials, as implemented in VASP [24, 25]. The plane-wave cutoff was 300 eV. We used an orthorhombic supercell with 360 atoms and sampled the Γ point. We then used DFT with the hybrid functional of Heyd, Scuseria, and Ernzerhof [26] to compare the stability of different charge states. We find that Ag_{int} is a donor with a binding energy of 0.10 eV, while Ag_{Cd} is an acceptor with a binding energy of 0.32 eV. Hence the stable charge states of Ag_{int} and Ag_{Cd} are +1 and -1, respectively, when the Fermi level falls inside a window of ~ 1.2 eV within the band gap of 1.85 eV. We assumed these conditions to hold throughout this study. CdSe native defects could in principle also be included in the model. However, we expect them to be less important than the impurities themselves and therefore do not include them here.

We also used DFT with the PBE functional to calculate the activation barriers for two important processes: diffusion of Ag_{int} and cation substitution $\text{Ag}_{\text{int}} \rightarrow \text{Ag}_{\text{Cd}} + \text{Cd}$. The calculations used the nudged-elastic-band method in a 96-atom supercell [27], and assumed the charge states discussed above along with a compensating uniform background. We find that Ag_{int} moves between interstitial sites with a small barrier of only 0.2 eV, consistent with the observed fast diffusion of Ag in CdSe [28, 29]. It is reasonable to assume that, at room temperature, Ag ions enter the NC from solution as Ag_{int} and then rapidly diffuse between interstitial sites [30]. We investigated several reaction pathways for cation substitution and found that the kick-out reaction [Fig. 1(a)] had by far the lowest activation barrier, 0.68 eV [32]. In this reaction, Ag_{int} moves onto a Cd site by displacing the Cd to an interstitial site. As a result, Ag_{Cd} and an interstitial Cd (Cd_{int}) are created. The stable charge state of Cd_{int} is +2 (donor binding energy 0.29 eV) and thus the reaction preserves total charge: $\text{Ag}_{\text{int}}^+ + \text{Cd}_{\text{Cd}}^0 \rightarrow \text{Ag}_{\text{Cd}}^- + \text{Cd}_{\text{int}}^{2+}$.

The final state of this reaction is only marginally stable because the reverse reaction has a very low barrier (0.06 eV). Consequently, after a kick-out step the system usually reverts to its initial state. Evidently, the cation-exchange process can proceed only if the Ag-Cd complex dissociates. This can occur if the Cd diffuses away, leaving behind Ag_{Cd} . Because the rate of this dissociation governs the overall cation-exchange rate, it is important to evaluate it under realistic conditions—that is, in small NCs containing many charged Ag impurities.

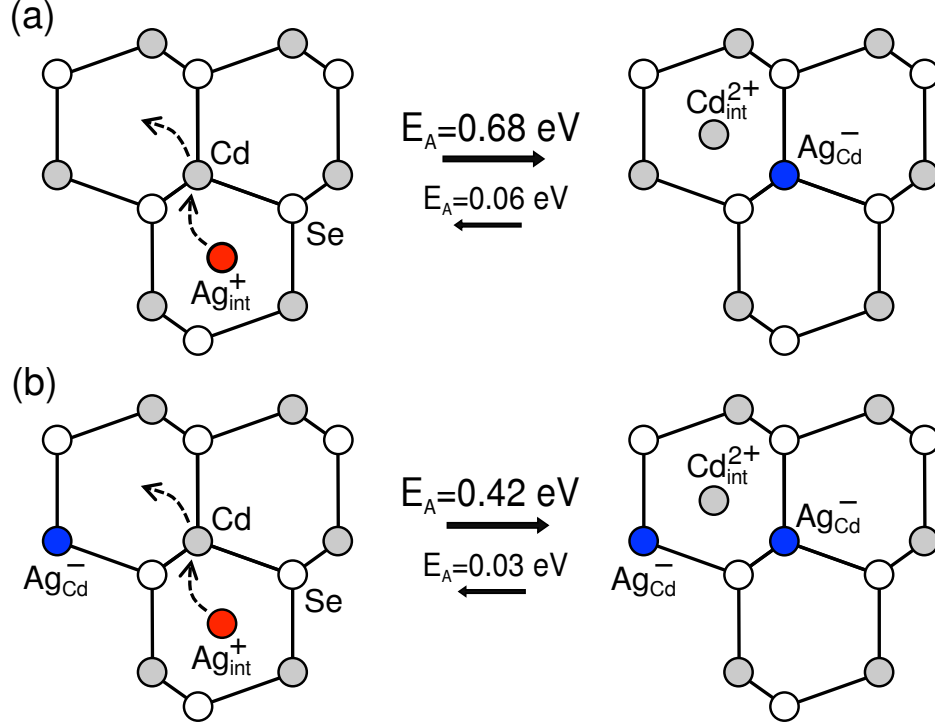


FIG. 1: Electrostatic reduction of the activation barrier for cation exchange. For cation exchange to occur, Ag ions must replace Cd ions on the CdSe lattice. (a) The pathway with the lowest activation barrier (0.68 eV in DFT) is the Cd kick-out reaction, in which an interstitial Ag_{int}^+ displaces a Cd, creating an interstitial $\text{Cd}_{\text{int}}^{2+}$ and a substitutional Ag_{Cd}^- . (b) The barrier for the Cd kick-out reaction is reduced (to 0.42 eV) if a substitutional Ag_{Cd}^- already occupies a neighboring site, because the arrangement of charges in the final state is then electrostatically favorable.

One consequence of confining ionized impurities to the small volume of a NC is that strong Coulomb interactions are inevitable. These profoundly affect the spatial distribution and reaction barriers of the impurities, and must therefore be included in a microscopic model. For example, if a NC contains several Ag_{int} with the same charge, then their mutual repulsion pushes them toward the NC surface. Each ion is also influenced by the polarization at the dielectric interface between the NC and the surrounding medium. Because the semiconductor dielectric constant is typically larger than its surroundings, this interaction is always repulsive and hence pushes the impurities toward the NC interior. The outcome of these competing interactions becomes more complicated when the dopants are of different types, are in different charge states, or occupy both interstitial and substitutional sites.

The importance of Coulomb effects is especially clear for Cd kick-out reactions. In the absence of other dopants, this reaction is energetically uphill with a substantial activation barrier (0.68 eV). For an attempt frequency of 10^{13} Hz [33], this barrier can be overcome at room temperature, but not at a rate consistent with the observed millisecond time scales [34]. Experiments suggest much higher rates and thus lower activation barriers. This puzzle is resolved by considering Coulomb interactions. If other ionized impurities are nearby, they can strongly alter the barrier for reactions in their vicinity. Indeed, we find using DFT that Coulomb interactions greatly reduce the barrier for kick out whenever the final state is favored by the arrangement of charges. In the best case, a nearby Ag_{Cd} lowers the barrier from 0.68 to 0.42 eV [Fig. 1(b)], because in the final state the $\text{Cd}_{\text{int}}^{2+}$ is located between oppositely charged (Ag_{Cd}^-) impurities. At room temperature this reduction increases the kick-out rate by a factor of 10^4 .

Coulomb interactions also drive the cation-exchange process on a larger scale, by favoring the formation of contiguous regions of electrostatically bound Ag_2 pairs (Ag_{int}^+ plus Ag_{Cd}^-) for each Se atom. *Thus, the cation-exchange reaction depends on a positive feedback arising from strong Coulomb interactions between charged impurities.* This conclusion agrees with experiments showing that cation exchange in NCs is a cooperative mechanism in which one event triggers an extremely fast transformation [35]. In our case, this event is the formation of the initial Ag_{Cd} , which we hypothesize occurs by Cd kick out at the NC surface. We also found using DFT [13] that such a fully substituted phase is crystallographically—as well as energetically—very close to the crystalline Ag_2Se naumannite phase, consistent with experiment [12].

Figure 2 summarizes the steps in our model. Ag ions enter the NC via interstitial pathways. Repelled from the surface by dielectric polarization, they diffuse towards the center. As the concentration increases, their mutual repulsion becomes dominant and drives them back towards the surface [Fig. 2(a)]. At this stage, the formation of Ag_{Cd} is likely to occur, for two reasons. (1) The formation of negatively charged Ag_{Cd}^- can compensate electrically for the positive charge accumulating near the surface due to the Ag_{int}^+ . (2) The Cd that is replaced by Ag can immediately leave the NC by diffusing into the surrounding solution, preempting the reverse kick-out reaction. Once Ag_{Cd}^- is formed, it attracts mobile Ag_{int}^+ [Fig. 2(b)] and, in addition, lowers the barrier for nearby kick-out reactions. Consequently, additional interstitial and substitutional Ag coalesces in the surface region around the nucle-

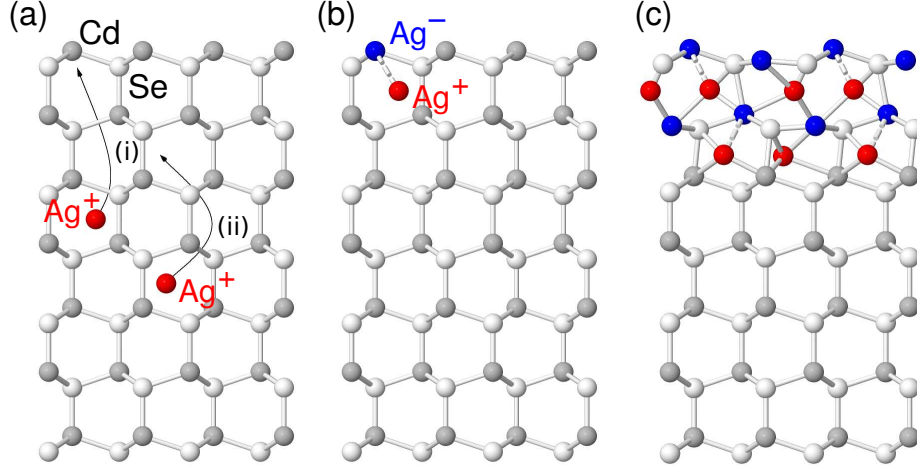


FIG. 2: Microscopic model of Ag doping and cation exchange of CdSe NCs. (a) At low concentration, Ag are highly mobile interstitial ions, Ag_{int}^+ . As their number increases, their mutual repulsion pushes them toward the NC surface (top) where a Cd kick-out reaction can occur [step (i)]. The substitutional Ag_{Cd}^- created by the kick-out reaction attracts the remaining Ag_{int}^+ [step (ii)]. (b) An electrostatically bound complex is then formed by two Ag at the surface, forming a nucleus of Ag_2Se . (c) At even higher Ag concentrations, all interstitial and Cd sites at the surface become occupied with Ag. This fully substituted CdSe closely resembles the naumannite crystal structure of Ag_2Se .

ating site [Fig. 2(c)]. The result is a stable and densely packed cluster of alternating charges, having the stoichiometry of Ag_2Se and an arrangement of atoms close to the naumannite structure, into which it easily relaxes.

To investigate our model quantitatively we used dynamical simulations based on the kinetic Monte Carlo (KMC) method [33], an efficient technique for simulating dynamics over long times at finite temperature. An initial random state was stochastically evolved by selecting from a list of processes (diffusion and kick-out reactions) using acceptance ratios given by their Boltzmann factors. These were evaluated using the DFT barriers already computed [36]. To account for Coulomb interactions, we added the state-dependent Coulomb potential from all ions to the reaction pathway for each process [37]. When the impurities were within approximately one lattice constant [as in Fig. 1(a)], these were included directly using DFT. For larger separations they were approximated using point charges and the CdSe

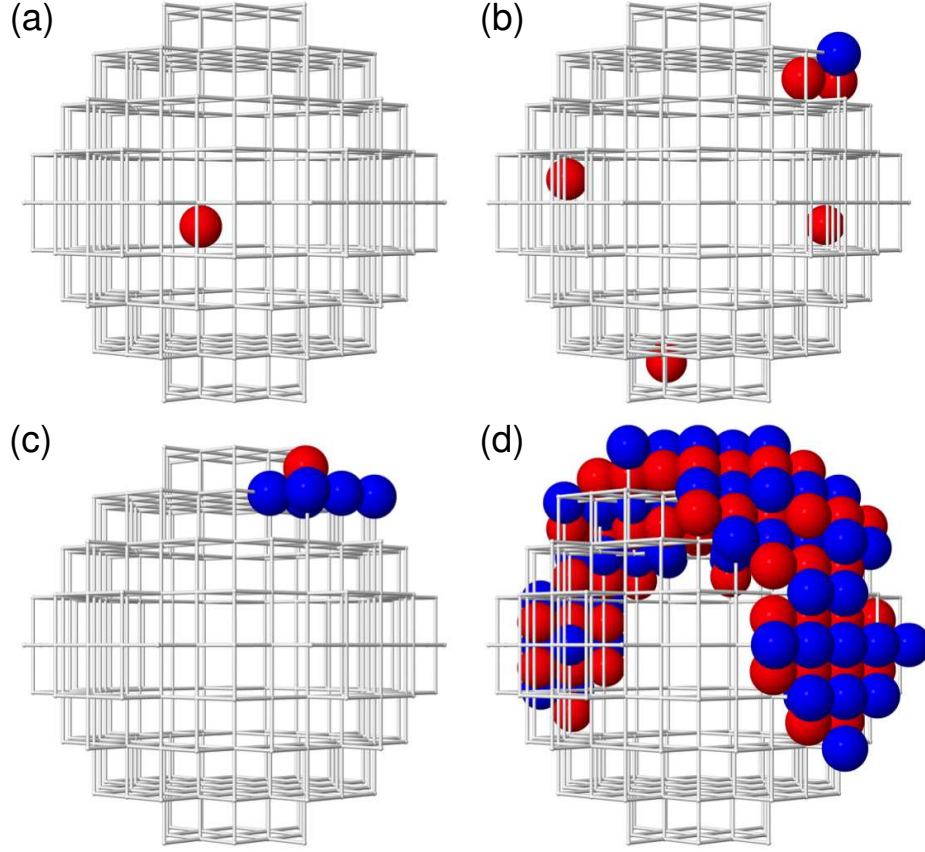


FIG. 3: Four stages of cation exchange, depicted by snapshots from KMC simulations at 300 K. Red and blue spheres denote Ag_{int}^+ and Ag_{Cd}^- , respectively. (a) With only one Ag_{int}^+ , the impurity stays near the NC center. (b) With additional Ag_{int}^+ , they repel each other toward the surface, where kick out of Cd by Ag can occur. (c) If no further Ag is added, the impurities eventually cluster at the surface, mostly as Ag_{Cd}^- . (d) Additional Ag leads to the growth of Ag_2Se at the surface.

dielectric constant. Interactions with polarization charges at the nanocrystal surface were included using an electrostatic model [38] of point charges in a dielectric sphere embedded in an organic medium.

We performed the simulations for a quasispherical NC with a realistic diameter of 3.5 nm [Fig. 3]. For simplicity we used a simple cubic lattice and set the density of Cd sites to that of wurtzite CdSe, giving a lattice constant of 3.9 Å. The Se atoms were included implicitly and considered immobile because they are known not to participate in cation exchange. Ag ions were added to the NC at interstitial sites on the surface. In the absence of any

Coulomb interactions, the reaction barrier for this step was set to 0.6 eV to yield reasonable addition rates for Ag. We also assumed that Ag_{int} did not leave the NC. In contrast, Cd_{int} was allowed to diffuse out, as is observed experimentally [3]; the driving force for this is the hard Lewis base (e.g. methanol or ethanol) that comprises the solution and which strongly binds to the hard Lewis acid Cd^{2+} . In the real system, Cd ions hence become solvated in solution; for simplicity we removed them from the simulation after they diffused out.

As Ag^{+1} ions enter and Cd^{+2} ions leave, the NC may become transiently charged. This charge must be balanced by counterions outside the NC. We assumed these to be mobile and thus treated them as uniformly spread out near the NC; hence they did not affect the potential-energy surface for reactions inside [13]. On average, two Ag^{+1} ions enter for each Cd^{+2} that leaves, and therefore the NC maintains approximate electrical neutrality as CdSe is converted to Ag_2Se .

Figure 3 shows snapshots from simulations at 300 K. Four different stages are depicted, from one Ag to a partially cation-exchanged NC with Ag_2Se formed near the surface. The simulations confirm that, due to the dielectric polarization discussed above, a single $\text{Ag}_{\text{int}}^{+}$ tends to stay in the NC center as a stable interstitial [Fig. 3(a)], whereas several $\text{Ag}_{\text{int}}^{+}$ push each other toward the surface and allow the formation of Ag_{Cd} [Fig. 3(b)]. If the supply of Ag_{int} is stopped at this stage, the simulation evolves to a configuration with a majority of Ag_{Cd} [Fig. 3(c)]. If further Ag is then provided, a well-defined Ag_2Se phase grows from the surface inwards [Fig. 3(d)]. Although we did not run the simulations to completion (due to their cubic dependence on the number of Ag ions) it is clear that, if continued, the nanocrystal would have been completely converted to Ag_2Se . A video animation of one simulation run is available in the Supplemental Material 13.

These simulations can be investigated more quantitatively by averaging over many runs. Figure 4 shows the Ag site occupancy as a function of radial position for NCs with one, two, and 150 Ag dopants. The results reflect the competition between opposing Coulomb effects. With a single Ag impurity, interstitial sites near the center are strongly favored, because dielectric polarization dominates the interactions. This is clear from comparing to the distribution predicted analytically [black curve in Fig. 4(a)]. With only one impurity, the formation of Ag_{Cd} is unlikely because Ag_{int} , despite being mobile, spends very little time near the surface. However, even with only two $\text{Ag}_{\text{int}}^{+}$, the ion-ion interactions change the shape of the concentration distribution [Fig. 4(b)]. With 150 Ag, both Ag_{int} and Ag_{Cd} are

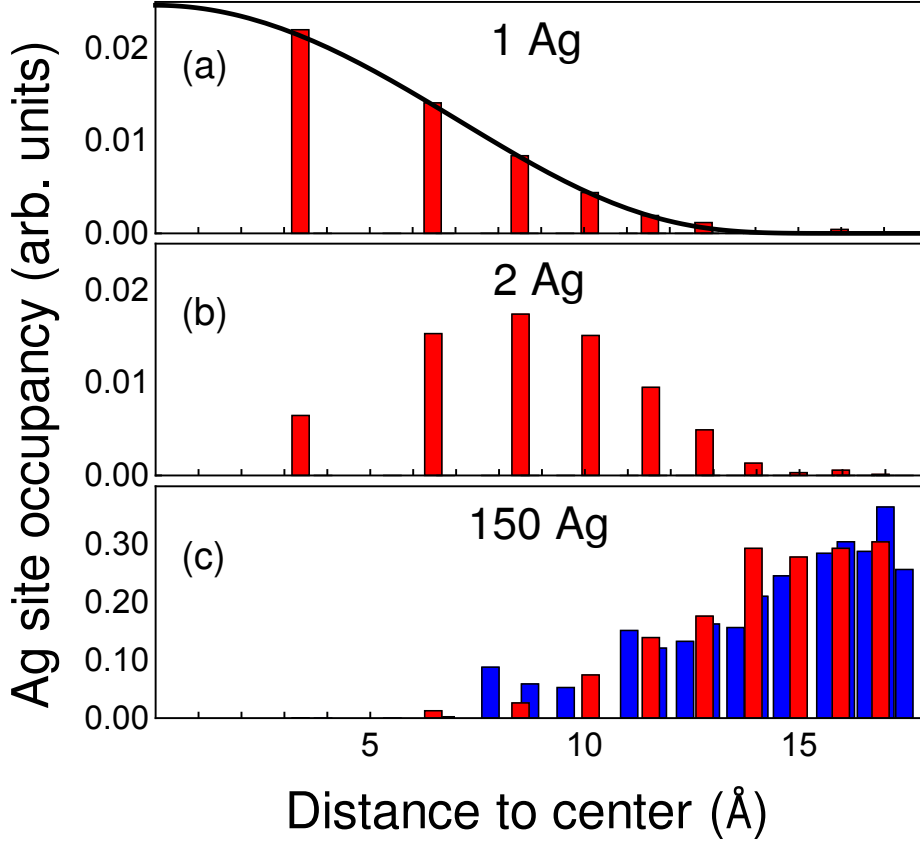


FIG. 4: Site occupancy at 300 K of Ag_{int} (red) and Ag_{Cd} (blue) versus radial distance from the center of the NC. The distributions are averages over 100 KMC simulations for (a) one, (b) two, and (c) 150 Ag impurities per NC. The black curve in (a) shows the Boltzmann distribution at 300 K based on the energy from dielectric polarization.

present and their concentration is greatest at the surface [Fig. 4(c)]. The two types of Ag are nearly equal due to the formation of Ag_2Se , because naumannite has two inequivalent Ag sites.

Our model is also consistent with two trends observed experimentally in Ag-doped CdSe NCs [10]. (1) The photoluminescence (PL) efficiency of undoped samples increased dramatically even when only one Ag was added per NC. Our simulations predict that a single Ag_{int}^+ preferentially occupies the NC center. This positive charge can influence the photoexcited exciton by pulling the electron away from the surface and suppressing nonradiative recombination. Moreover, the PL efficiency decreased with further Ag incorporation, consistent with the predicted redistribution of Ag toward the surface. (2) Electrical transport measure-

ments on doped NC films showed an increase and then a decrease in the Fermi level when the number of Ag per NC was varied from zero to 20. This was attributed to a change of the Ag from interstitial donors to substitutional acceptors at ~ 7 Ag per NC [10]. Our results confirm that at low concentration, Ag persists as an interstitial donor and is easily ionized to provide free electrons. At higher Ag concentrations the majority become substitutional acceptors [Fig. 3(c)]. Thus, our simulations are consistent with the observed nonmonotonic dependence of the Fermi level on Ag incorporation. Finally, at higher concentrations, Ag_2Se starts to form at the surface, and the behavior of the Fermi level becomes more complicated.

In summary, we have proposed a microscopic model of Ag cation exchange in CdSe NCs. The key mechanisms—interstitial diffusion, cation kick out, impurity-impurity Coulomb interactions, and NC surface polarization—are quite general and therefore likely relevant to other cation-exchange systems, such as Cu in CdE. Furthermore, because more complex situations with mixed electrically active dopants can now be treated, we anticipate that new and unexpected phenomena will arise when these principles are applied to other NC systems.

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and hence growth and doping occur concurrently [31]. In arrested cation exchange, however, the growth is performed first and only then are dopants added to the solution. To dope the NC, they must enter through its surface—most likely via interstitial pathways.

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